

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 13/06, 13/00	A1	(11) International Publication Number: WO 96/16913 (43) International Publication Date: 6 June 1996 (06.06.96)
<p>(21) International Application Number: PCT/EP95/04730</p> <p>(22) International Filing Date: 30 November 1995 (30.11.95)</p> <p>(30) Priority Data: P 44 43 022.1 2 December 1994 (02.12.94) DE</p> <p>(71) Applicant (for all designated States except US): ISOVER SAINT-GOBAIN [FR/FR]; Les Miroirs, 18, avenue d'Alsace, F-92400 Courbevoie (FR).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): LOHE, Peter [DE/DE]; Rüterstrasse 5, D-67122 Mutterstadt (DE). HOLSTEIN, Wolfgang [DE/DE]; Herderstrasse 2, D-35315 Homberg (DE). SCHWAB, Wolfgang [DE/DE]; Schönaauer Strasse 25, D-68723 Plankstadt (DE).</p> <p>(74) Agent: KADOR & PARTNER; Corneliusstrasse 15, D-80469 Munich (DE).</p>		<p>(81) Designated States: AU, BR, CA, CN, CZ, FI, HU, IS, JP, KR, NO, NZ, PL, SI, SK, US. European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: A MINERAL FIBER COMPOSITION</p> <p>(57) Abstract</p> <p>A biodegradable mineral fiber composition, characterized by the following constituents in percent by weight: SiO₂: 45 to 55; Al₂O₃: 0 to less than 4; Fe₂O₃: more than 7 to 15; CaO: 18 to 35; MgO: 5 to 15; Na₂O+K₂O: 0 to 10; P₂O₅: 0 to 5; impurities: 0 to 2.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Larvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

A mineral fiber composition

This invention relates to a mineral fiber composition which is biodegradable, i.e. the fibers decompose as soon as they come in contact with a physiological milieu.

The prior art already describes some mineral fiber compositions which are said to be biodegradable.

Biodegradability of mineral fiber compositions is of great importance since various studies indicate that mineral fibers with very small diameters in the range of under 3 microns are suspected to be carcinogenic, while biodegradable mineral fibers with such dimensions show no carcinogenicity.

However, mineral fiber compositions must also have good workability by known methods for producing mineral wool with a small diameter, in particular the jet process or the external rotary process. This involves in particular a sufficient difference of e.g. 80° between the devitrification and processing temperatures.

The mechanical and thermal properties of mineral fibers, or the products made therefrom, are also of crucial importance. Mineral fibers are used for example for insulating purposes to a great extent. Sufficient temperature resistance of the mineral fibers is necessary in particular for use in the industrial sector.

The problem of the invention is to provide a novel mineral fiber composition which is distinguished by high biodegradability, has sufficient temperature resistance for application in the industrial sector, and can be fiberized well.

The invention is based on the finding that this problem can be solved by a mineral fiber composition which consists substantially of silicon dioxide and alkaline-earth oxides,

and further contains alkali oxides as a melting accelerator and a considerable proportion of iron oxide for increasing temperature resistance.

It has turned out that such mineral fiber compositions fulfill the combination of necessary properties, namely biodegradability, sufficient temperature resistance for insulated objects in industry, as well as good workability in the production of the mineral wool as such and the products. This simultaneously means that the upper devitrification temperature of the melt is preferably under 1300°C.

The subject of the invention is a mineral fiber composition which is biodegradable, characterized by the following constituents in percent by weight:

SiO ₂	45 to 55
Al ₂ O ₃	0 to less than 4
Fe ₂ O ₃	more than 7 to 15
CaO	18 to 35
MgO	5 to 15
Na ₂ O + K ₂ O	0 to 10
P ₂ O ₅	0 to 5
Impurities	0 to 2

The inventive mineral fiber compositions are readily drawable in particular by the jet process, i.e. one obtains a mineral wool with a low-shot content.

The mineral fibers reach a high temperature resistance of at least 1000°C according to DIN 4102, part 17.

Such mineral fibers show good biodegradability.

The mean fiber diameter is usually 1 to 15 microns, a range of 2.5 to 8 microns being preferred.

The addition of alkali oxides causes a melting point reduction and therefore better workability in the melting process. Furthermore, up to 30% recycled glass can be used advantageously with a sodium-containing mineral wool composition.

The inventive mineral fiber compositions can preferably be melted in melting chambers fueled with fossile fuels, in particular natural gas, at melting temperatures from 1350 to 1450°C. Such melting chambers can produce a homogeneous melt, which is a prerequisite for constant product quality. Homogeneity of the glass melt also facilitates the reproducibility of the fiberizing process and thus of the thermal and mechanical product properties. Furthermore, the constant chemical composition of the thus produced mineral wool leads to controllable biodegradability.

In particular the addition of iron oxide increases the temperature resistance of the mineral wool.

The inventive mineral fiber compositions preferably have the following constituents in percent by weight:

SiO ₂	45 to 53
Al ₂ O ₃	0.3 to 3.9
Fe ₂ O ₃	more than 7 to 13
CaO	20 to 25
MgO	10 to 15
Na ₂ O + K ₂ O	3 to 8
Impurities	0 to 2

A content of silicon oxide in the range of 46 to 52% by weight is especially preferred.

With respect to the alkali oxides a range of 3 to 6% by weight is especially preferred. Iron oxide is preferably present in a range between 7,1 and 11% by weight.

To assess biological degradability the standard powder test of the German Glass Society was used. This is an easily conducted method and gives a sufficient measure of biological degradability when used with a simulated physiological lung fluid at 37°C. The method is described in L. Springer, "Laboratoriumsbuch für die Glasindustrie", 3rd edition, 1950, Halle/S: W. Knapp Verlag.

The thermal behavior of the mineral fibers was determined by the so-called "Swedish method". This method uses a silit pipe furnace with a horizontal working pipe open on both sides with a length of 350 mm and an inside diameter of 27 mm. In the center of the furnace there is a ceramic supporting plate with dimensions of 30 x 20 x 3 mm for positioning the test sample. The test sample has dimensions of 12 x 12 x 12 mm or 12 mm \varnothing x 12 mm height. The gross density is normally 100 kg/m³. The temperature increase is 5 K/min. The change in test sample height is determined continuously with a reading optic.

The invention will be described more closely in the following using examples.

Example 1

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	47.4
Al ₂ O ₃	0.6

Fe ₂ O ₃	10.1
CaO	23.5
MgO	10.4
Na ₂ O	7.4
K ₂ O	0.3
Diverse	0.3

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

An investigation by the modified powder test of the Deutsche Glasgesellschaft yielded a value of 45 mg/kg and thus a value for high biodegradability.

Determination of thermal behavior by the "Swedish method" yielded a temperature resistance of 950°C with 20% height reduction, which can be clearly seen in the corresponding diagram shown by way of example in the single drawing.

Example 2

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	49
Al ₂ O ₃	0.3
Fe ₂ O ₃	10.0
CaO	23.5
MgO	12

Na ₂ O	5.5
Diverse	0.2

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a mean diameter range of 2.5 to 8.0 microns.

An investigation by the modified powder test of the Deutsche Glasgesellschaft yielded a value of 42 mg/kg and thus a value for high biodegradability.

Determination of thermal behavior by the "Swedish method" yielded a temperature resistance of 1000°C with 20% height reduction.

Example 3

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	48.7
Al ₂ O ₃	0.5
Fe ₂ O ₃	10.0
CaO	23.1
MgO	11.9
Na ₂ O	5.4
K ₂ O	0.1
Diverse	0.3

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into

mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Example 4

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	49.7
Al ₂ O ₃	0.5
Fe ₂ O ₃	9.0
CaO	23.1
MgO	11.9
Na ₂ O	5.4
K ₂ O	0.1
Diverse	0.3

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Example 5

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	50.7
Al ₂ O ₃	0.5

Fe ₂ O ₃	8.0
CaO	23.1
MgO	11.9
Na ₂ O	5.4
K ₂ O	0.1
Diverse	0.3

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Example 6

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	51.7
Al ₂ O ₃	0.5
Fe ₂ O ₃	7.1
CaO	23.1
MgO	11.9
Na ₂ O	5.4
K ₂ O	0.1
Diverse	0.2

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Example 7

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	51.7
Al ₂ O ₃	0.5
Fe ₂ O ₃	7.1
CaO	25.5
MgO	11.9
Na ₂ O	3.0
K ₂ O	0.1
Diverse	0.2

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Example 8

A mineral wool was produced with the following composition in percent by weight:

SiO ₂	46.0
Al ₂ O ₃	2.5
Fe ₂ O ₃	7.1
CaO	27.5
MgO	13.3

Na ₂ O	3.0
K ₂ O	0.1
Diverse	0.5

This composition could be readily fiberized by the jet process at a drawing temperature between 1300 and 1400°C into mineral fibers with a diameter range of 1.0 to 15 microns, a mean diameter range of 2.5 to 8.0 microns being preferred.

Claims

1. A mineral fiber composition which is biodegradable, characterized by the following constituents in percent by weight:

SiO ₂	45 to 55
Al ₂ O ₃	0 to less than 4
Fe ₂ O ₃	more than 7 to 15
CaO	18 to 35
MgO	5 to 15
Na ₂ O + K ₂ O	0 to 10
P ₂ O ₅	0 to 5
Impurities	0 to 2

2. The mineral fiber composition of claim 1, characterized by the following constituents in percent by weight:

SiO ₂	45 to 53
Al ₂ O ₃	0.3 to 3.9
Fe ₂ O ₃	more than 7 to 13
CaO	20 to 25
MgO	10 to 15
Na ₂ O + K ₂ O	3 to 8
Impurities	0 to 2

3. The mineral fiber composition of claim 1 or 2, characterized in that the proportion of silicon dioxide is 46 to 52% by weight.

4. The mineral fiber composition of any of claims 1 to 3, characterized in that the alkali oxides are present in a quantity of 3 to 6% by weight.

5. The mineral fiber composition of any of claims 1 to 4, characterized in that iron oxide is present in a content between 7 and 11% by weight.

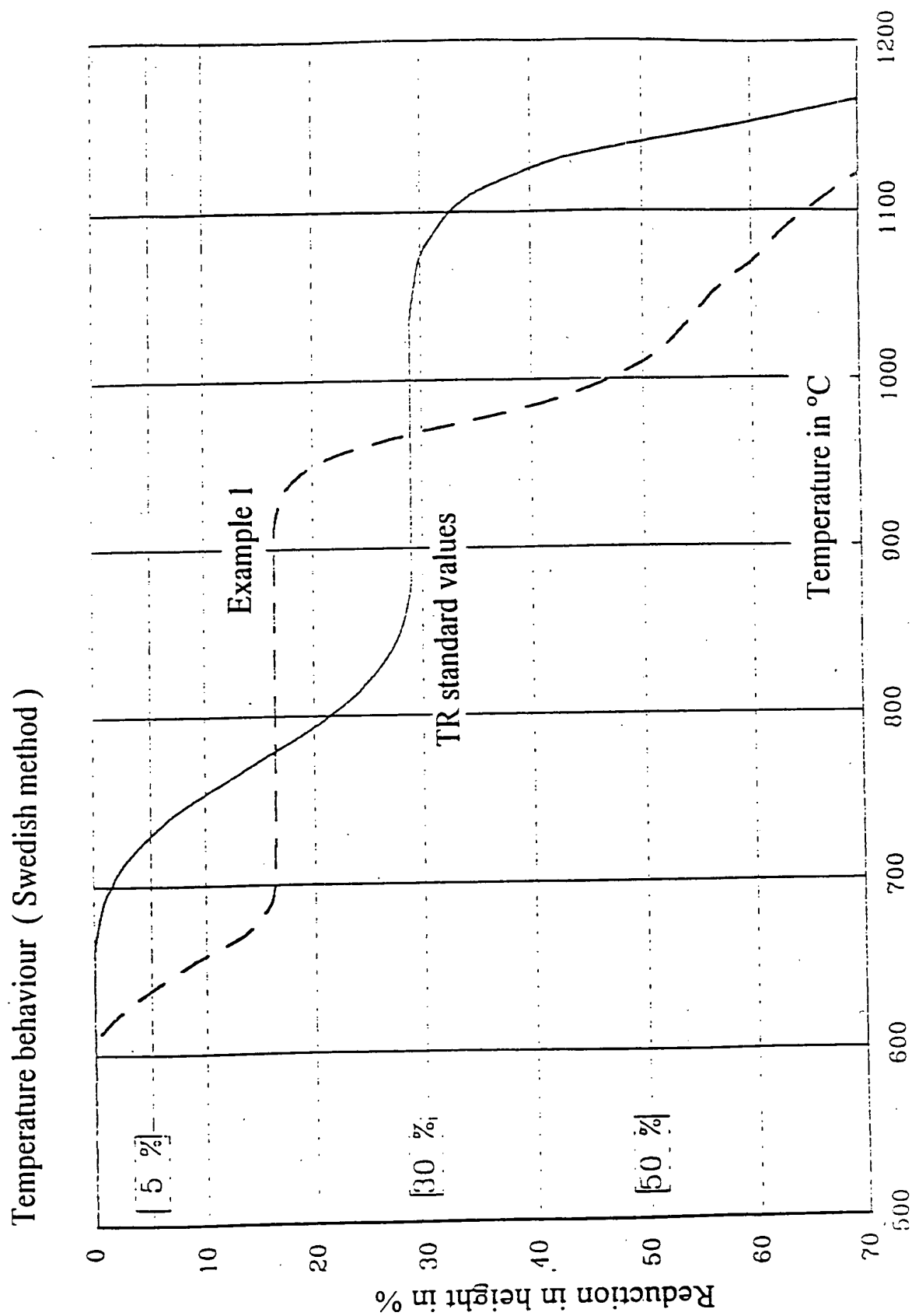


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.

EP 95/04730

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C13/06 C03C13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 22251 (ISOVER SAINT-GOBAIN) 11 November 1993 see page 1, line 37 - page 4, line 3; examples 12,13; tables 1,4	1-5
X	WO,A,94 14717 (ROCKWOOL INTERNATIONAL A/S) 7 July 1994 see page 3, line 3 - line 20; table 1	1,5
A	-----	2-4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* "&" document member of the same patent family

Date of the actual completion of the international search

20 March 1996

Date of mailing of the international search report

- 2. 04. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

on on patent family members

Inter. Application No

EP 95/04730

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9322251	11-11-93	FR-A- 2690438	29-10-93
		AU-B- 4263293	29-11-93
		BR-A- 9305492	11-10-94
		CA-A- 2110998	11-11-93
		CN-A- 1078708	24-11-93
		CZ-A- 9302865	19-10-94
		EP-A- 0596088	11-05-94
		HU-A- 67212	28-03-95
		JP-T- 6508600	29-09-94
		NO-A- 934725	20-12-93
		SI-A- 9300218	31-12-93
		SK-A- 146893	09-11-94
		ZA-A- 9302874	01-06-94
WO-A-9414717	07-07-94	AU-B- 5831694	19-07-94
		CA-A- 2152920	07-07-94
		EP-A- 0677026	18-10-95
		PL-A- 309641	30-10-95